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NONEQUILIBRIUM DEFECTS IN GLASS AND THEIR ROLE IN CRYSTALLIZATION PROCESSES (A REVIEW)

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A possible mechanism of the effect of nonequilibrium defects (dislocations) on crystallization of glasses is described. The effect of precrystallization and crystallization processes on the activity of glass and glass ceramic phase in synthesis of composite materials in hydrothermal conditions is established.

A characteristic feature of solid bodies is the fact that their reactivity is not uniquely determined by their chemical and phase composition [1, 2]. Therefore, in order to specify the reactivity of a reactant in a specific process, researchers often use the concept of activity and activation, which are directly related to the existence and formation of nonequilibrium defects [1]. The latter is obvious with respect to crystals; however, concerning materials in the amorphous (vitreous) state, there is yet no unique answer. The production technology of composite materials for construction implies that the activity of a solid-phase material is related to its internal energy, which is higher in the vitreous state than in the crystallized state of the same composition [3 – 5]. However, in certain processes, the reactivity of crystalline and amorphous bodies can be comparable, whereas the properties of the vitreous phase to a large extent depend on its thermal history and the respective structural modifications.

Any structural transformations in amorphous materials result in significant modifications of virtually all properties [3, 6]. The glass structure is modified as the glass passes to more stable states, and the structural transformations can either proceed without modification of the phase composition of the glass or become phase transformations, i.e. liquation and crystallization [7]. One can assume that the activity and the reacting capacity of glass and crystal to a great extent can be related to the existence and interaction of nonequilibrium defects, especially dislocations. The nonequilibrium defects produce the greatest effect on the processes of silicate formation, sintering, for instance, in production of ceramic materials and glass ceramics using powder technology, and on the synthesis of materials in hydrothermal conditions, for example, the production of silicate concrete.

There are several known dislocation theories and models in which an increase in the dislocation density is regarded as the main reason for the disturbance of the far order in crystals (melting or rendering amorphous) [8 – 11]. There are indirect experimental data which point to the existence of dislocations of the atomic scale, for example, in metallic glasses [12]. At the same time, it is noted that glass in the hardened state has an extremely high dislocation density. Whereas in crystals, the Burgers vector, which serves as the medium distortion measure near a dislocation, is constant and well retained for a particular gliding system, the same vector in amorphous solids, as a rule, is a variable vector along the dislocation line [13].

A dislocation model was offered in [14], which accounts for interaction between the dislocations even in highly deformed crystals and describes the activation properties of materials, starting with a perfect crystal and ending with amorphous or completely destroyed material with broken chemical bonds. Figure 1 represents a generalized dependence of dislocation formation energy converted to one interatomic distance on the dislocation density, which is calculated for a perfect (primitive) cubic lattice [14]. In this case, the dislocation formation energy is an indirect characteristic which makes it possible to estimate the potential capacity of a solid-phase material for structure modifications in a specific activation process. It is possible to distinguish three ranges of existence of solid-phase materials in the curve shown in Fig. 1. The first region corresponds to crystal materials with a low dislocation density typical of most natural materials (around $10^6 - 10^8 \text{ cm}^{-2}$). Within this region, introduction of each subsequent dislocation weakens the bonds in the crystal lattice and increases the reactivity of the material in thermochemical or hydrothermal reactions [15].

With the volume density of dislocations equal to 10^{25} m^{-3} , the crystalline state can be transformed into the

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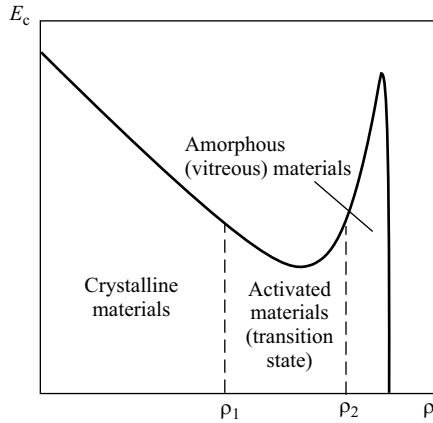


Fig. 1. Dependence of the energy of formation of a dislocation length unit (converted to interatomic distance) of solid-phase materials on the dislocation density.

amorphous state [9, 10], which, depending on the crystal lattice parameters, correlates with the dislocation density around $10^{10} - 10^{13} \text{ cm}^{-2}$. The minimum dislocation formation energy in Fig. 1 is observed precisely under this degree of deformation of the crystal lattice. The materials with such dislocation density can be arbitrarily distinguished as a separate group of activated materials in the transition state. The activity and reactivity of these materials are not uniquely determined by the dislocation density and to a great extent are related to the structure of the emerging dislocation ensembles. In this case, the activated materials are often characterized by the defects arising at the mesoscopic level ($0.1 - 3 \mu\text{m}$), which is the main range in which the collective dislocation effects are manifested [16].

Consequently, the defect-forming processes in crystalline materials lead to the formation of activated materials (Fig. 1) which may have structural disturbances at the mesoscopic level. As a result of the emergence of mesoscopic disturbances and the rearrangement of the defect structure at the mesoscopic level, the activity of the material can be significantly altered and have a substantial effect on the synthesis and the physicochemical properties of composites produced in hydrothermal conditions and in firing [17].

The further processes of defect formation in activated materials lead to their transformation into the amorphous (vitreous) state. As a result of interaction between the dislocations, the energy needed for the formation of dislocations starts increasing, that is, the potential capacity of the solid phase for structural modifications becomes slightly weaker (Fig. 1). In the context of the proposed dislocation model [14], amorphous materials can exist in a metastable state (the curved segment in the region of the existence of amorphous bodies, which is characterized by increased dislocation formation energy per dislocation length unit) or in the unstable state (the curve segment characterized by abrupt drop in the dislocation formation energy from the maximum to zero). The latter state can be presumably reached under special

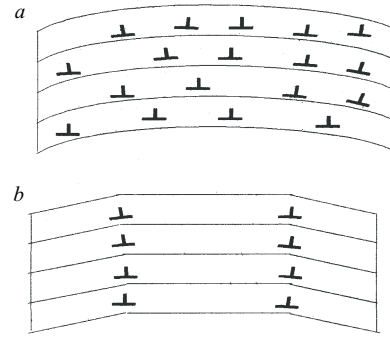


Fig. 2. Scheme of polygonizing in a crystal: *a*) chaotic arrangement of edge dislocations \perp in a curved crystal; *b*) vertical walls made of dislocations after polygonizing (the elastic stress fields of single dislocations in the wall to a great degree become mutually annihilated, since the compression area of one dislocation is located under the tension area of another dislocation).

conditions with a high degree of material deformation, for instance, using the Bridgman anvil [18].

Thus, study of the proposed dislocation model suggests that whereas the activity of a crystal grows due to its increased degree of defects, the activity of a metastable vitreous phase can be enhanced by rearrangement of the glass structure.

Similar to the process of rearrangement of dislocation structures observed in crystalline materials under thermal polygonizing (the process leading to a redistribution of dislocations and the formation of randomly shaped areas in the crystal, which are free of dislocation and subdivided by low-angle subboundaries; Fig. 2) [19, 20], the restructuring processes in glass may be related to the formation of crystal seeds. An arbitrary model of such restructuring is shown in Fig. 3. At the same time, it is noted in [20] that in some cases it may happen that the subboundaries in crystals do not reach the state corresponding to the minimum of energy. As a result, unstable configurations of gradient subboundaries are formed. Figure 3*b* shows a possible example of the formation in glass of a crystal seed with an imperfect boundary arising under the effect of stresses. As a result, the processes of nucleation, annihilation, and growth of seeds and their subsequent transformation into stable crystals may be directly related to the formation of primary subboundaries and their subsequent transformation into stable low-angle and large-angle phase boundaries.

However, a purely dislocation model cannot fully represent the real picture of the structural situations occurring in glass in the precrystallization period and during crystallization. The seed formation process in glass is implemented through the emergence of unstable fluctuations of the composition, their subsequent or simultaneous ordering, and further modification of the composition, which transforms these fluctuations into stable crystal seeds [21, 22]. It can be assumed that a parallel process is the formation of “seeds” of nonequilibrium defects, the structural rearrangement of the

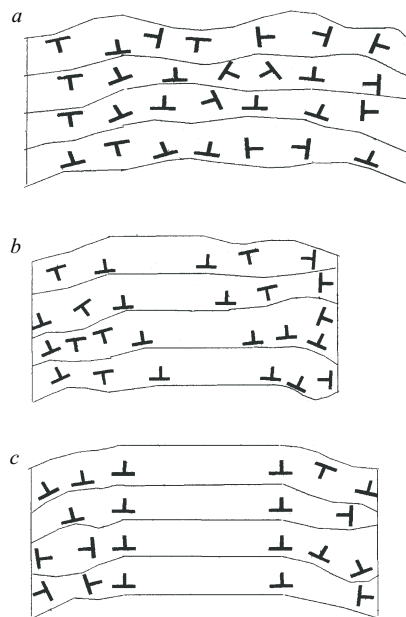


Fig. 3. Nonequilibrium dislocation structures in glass: *a*) initial glass; *b* and *c*) formation of a crystal seed with unstable and stable subboundaries, respectively.

system related to the emergence of dislocations, and later on, the appearance of subboundaries and phase boundaries in the glass. It is probably this circumstance that prompts the doubts of some researchers in the practical existence of homogenous seed formation [23].

Consequently, not only the formation of temporarily ordered areas in glass, but also the emergence of local segments of structurally nonequilibrium defects and their reorganization and interaction can serve as the basis for the process of formation of seeds or crystallization centers.

It is rather difficult to substantiate this assumption using direct methods of study, since the majority of the standard methods used to register dislocations in solids are not effective in the case of amorphous and vitreous bodies [13]. That is why several methods of indirect observation were used:

- the acoustic emission method [24, 25];
- direct methods of studying the glass structure defects (optical and electron microscopy) at the mesoscopic level, which is the main region in which collective dislocation effects (subboundaries, phase boundaries, etc.) are manifested [16];
- studying the activity of vitreous and glass ceramic materials in hydrothermal conditions, when the mobility of dislocations is sufficiently high [15].

The studies were performed on the basis of industrially produced glasses of wollastonite composition used to produce slag glass ceramics B-12 (white) and AS-2 (gray) at the Avtosteklo factory (Konstantinovka). The glasses were well annealed and produced in stable production conditions using the method of rolling a glass band 8 mm thick. The glasses had similar chemical compositions (%): 20.0–23.0 CaO,

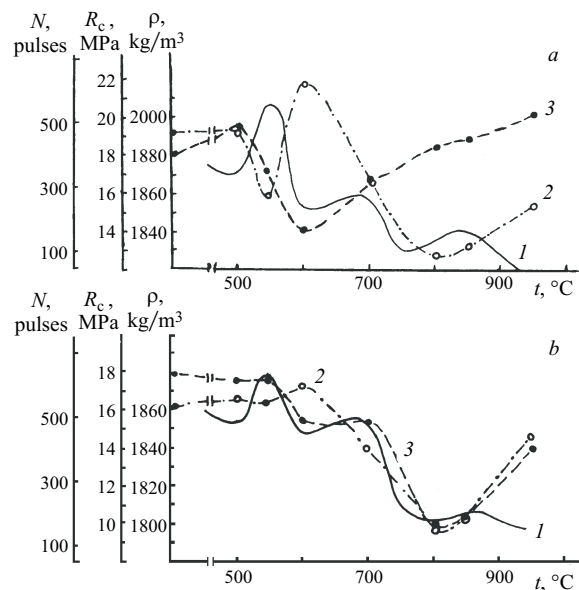


Fig. 4. Dependence of acoustic emission signals of glasses B-12 (*a*) and AS-2 (*b*) and the physicochemical parameters of silicate composites based on these glasses on the temperature of preliminary heat-treatment of glass: *1*) acoustic emission signals of glasses *N*; *2* and *3*) compressive strength R_c and density ρ of silicate composites.

0.8–15.0 MgO, 55.0–60.0 SiO₂, 5.0–8.0 Al₂O₃, 0.5–1.5 Fe₂O₃. The distinction consisted in the fact that B-12 glass composition additionally included 0.5–2.5% ZnO and a mixture of alkaline metal oxides – 3.0% Na₂O and 3.5–10.0% K₂O (AS-2 glass composition only contained Na₂O in an amount of 3.0–6.0%).

The glass samples were studied employing the methods of optical and electron microscopy and x-ray phase analysis. The temperature dependences of the total count of acoustic emission signals were obtained for the industrial glass samples within the temperature interval of 400–1000°C. Furthermore, the effect of the temperature of preliminary treatment of glasses on their reactivity in the conditions of hydrothermal synthesis was investigated. The samples of the initial and heat-treated glass were crushed to an equal specific surface area, with particle size below 315 μm. The crushed glass (glass ceramic) which served as the siliceous component of the silicate composite with 10% additive of slaked lime at the moisture level 8% was used to mold cylindrical samples 30 mm in height and 30 mm in diameter at the molding pressure 20 MPa. The samples were treated in an autoclave using the 1.5 + 6 + 1 h procedure with steam pressure 1.0 MPa. The activity of glasses AS-2 and B-12 was investigated under temperatures corresponding to the minimum and the maximum points on the acoustic emission curve.

The studies revealed extremum type of dependences of acoustic emission in glass and glass ceramics, as well as of the physicochemical parameters of silicate composites

based on these materials on the temperature of pretreatment of glass (Fig. 4) It should be noted that the introduction of zinc oxide to the slag glass ceramic composition (slag glass ceramic B-12) significantly increases the intensity of the modification of properties, which is typical both of acoustic emission and of the physicomechanical parameters of the composite materials obtained on the basis of the considered glasses.

According to the x-ray phase analysis data, the crystal phase could be observed for the first time only after treatment at 700°C. In this context, it can be assumed that the modification of the considered glass properties at temperatures below 600°C is mainly related to the structural changes in the vitreous phase and to a lesser extent to the crystallization processes. The strength parameters of silicate composites produced from the initial glass and the glass heat-treated at 500°C are virtually equal. The acoustic emission curve exhibits its first maximum at 550°C, which characterizes the maximum tension of the vitreous phase caused by the presence of composition fluctuations and nonequilibrium defects. However, the silicate composite which is based on the considered glass heat-treated at the specified temperature shows a certain decrease in strength and density. This can be evidence of some weakening of bonds and loosening of the vitreous phase structure, which is manifested in the properties of the obtained composite material.

At the temperature 600°C, a minimum is registered on the acoustic emission curve, which points to the continuing structural transformations of nonequilibrium defects. It can be assumed that the relaxation of stresses took place upon the formation of new linear defects and dislocation ensembles. At the same time, an increase in the reactivity of the vitreous phase has a significantly greater effect on the strength of the resulting composite, than the loosening of the glass structure caused by nonequilibrium defects. Thus, the strength of the samples reaches its maximum value, and their density decreases. At the same time, the structural quality coefficient A ($A = R_c / \rho^2$) of the composite material produced on the basis of heat-treated glass is 9 – 20% higher than the same parameter in the samples based on the initial glasses AS-2 and B-12.

The optical investigations were performed using crushed glass particles of size 10 – 30 μm at the magnification $\times 1000$ (using immersion oil), and the studies using direct dot electron microscopy were carried using sample fractures polished and pickled in 40% hydrofluoric acid. It was found that a continuous secondary structuring process in the vitreous phase is registered in the glass heat-treated at a temperature below 600°C. This process is characterized by the emergence of disturbances on the mesoscopic (0.1 – 3 μm) level, i.e., the dislocation substructure level [16, 17]. Although the applied methods only registered the secondary defects of the structure, which arise in the crushing stage or in polishing and pickling of glass, they provide indirect evidence of the

presence of disordered areas characterized by the presence of structurally nonequilibrium defects.

Further heat treatment of glasses at 700°C and over, intensified the process of origination and growth of crystals. The majority of linear defects, including free dislocations, are found in the composition of the phase boundary surface between the crystalline and the vitreous phase, which significantly deteriorates the reactivity of the solid phase and is accompanied by a nearly linear decrease in the strength of the silicate composite. At the same time, the coefficient A of the composite material decreases (with the preliminary heat treatment temperature 800°C) by 30 – 50%, compared to the parameters of the samples based on initial glass. The increase in the composite strength after 800°C may be related to the increased volume of the crystal phase inside the glass ceramic material and a certain metastability of the residual glass and the crystal phase.

Thus, the nonequilibrium defects can have a significant effect on the precrystallization and crystallization processes in glass, as well as on the vitreous phase activity, and should be taken into account in the development of respective composite materials.

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